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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-
POUNDS.

SEVENTH PAPER.

ORTHOBROMBENZYL COMPOUNDS.

BY C. LORING JACKSON AND J. FLEMING WHITE.

Presented November 12, 1879.

THE substances described in this paper are the first substituted benzyl compounds belonging to the ortho series known; unless, indeed, the orthochlorbenzaldehyde, made from salicylic aldehyde,* be included in this class. They were made from the orthobrombenzylbromide,† which was described in the first paper of this series as an oily liquid that did not solidify even at -15° . The specimen on which that experiment was tried could not have been perfectly pure, as we have since found that the orthobrombenzylbromide solidifies near zero in large rhombic crystals, often one centimeter in diameter, which melt at $30\frac{1}{4}^{\circ}$, and can be recrystallized from alcohol or ligroine. An analysis gave the following result:—

0.3570 gr. of substance gave 0.5380 gr. AgBr.

	Calculated for $C_7H_6Br_2$.	Found.
Bromine	64.00	64.13

Orthobrombenzylalcohol, $C_6H_4BrCH_2OH$, was made by the action of aqueous ammonia at 160° in a sealed tube on the acetate obtained by boiling the bromide with an alcoholic solution of sodic acetate. As its melting-point (80°) was much higher than expected, we also prepared

* Henry, Ber. d. ch. G., 1869, p. 136.

† These Proceedings, Vol. XII. p. 217.

it by heating the acetate with alcoholic potassic hydrate in a sealed tube, and by boiling the bromide with water for two days; and found that the products of all these methods melted at the same point (80°), so there can be no doubt that this is the true melting-point of the alcohol. An analysis of the substance made by the first method gave the following results:—

0.5543 gr. of substance dried *in vacuo* gave on combustion 0.9131 gr. CO_2 and 0.1990 gr. H_2O .

0.3480 gr. gave, by the method of Carius, 0.3498 AgBr.

	Calculated for $\text{C}_7\text{H}_6\text{BrOH}$.	Found.
Carbon	44.92	44.94
Hydrogen	3.74	3.99
Bromine	42.79	42.78

Properties. Slightly flattened white needles, sometimes 5 cm. long, when crystallized from boiling water, from ligroine needles grouped in sheaves, with but little odor, which melt at 80° , sublime in oily drops, and distil with steam very easily. It is very slightly soluble in cold, much more so in hot water or ligroine, and freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It can be most conveniently purified by crystallization from hot ligroine. Oxidized with potassic permanganate, it gave orthobrombenzoic acid, melting point 147° – 148° .

The *Orthobrombenzylcyanide*, prepared by boiling alcoholic potassic cyanide with the bromide, was a dark-colored oil, which did not solidify in a freezing mixture, and seemed to be decomposed by distillation; we therefore did not attempt to purify and analyze it.

The *Orthobromalphatoluylic Acid*, $\text{C}_6\text{H}_4\text{BrCH}_2\text{COOH}$, was made from the cyanide by heating it with strong hydrochloric acid to 130° in a sealed tube. The product was purified by conversion into the ammonium salt, and recrystallization from water or alcohol of the acid set free from this by dilute sulphuric acid.

It forms white pearly plates, or flattened needles, melting at $102\frac{1}{2}^{\circ}$ – 103° ; but little soluble in cold, more so in hot water, freely in alcohol, ether, benzol, glacial acetic acid, and carbonic disulphide. It is only sparingly soluble in cold ligroine, but very soluble in hot, from which it crystallizes in small needles arranged in fan-shaped groups.

Argentie Orthobromalphatoluylate, $\text{C}_6\text{H}_4\text{BrCH}_2\text{COOAg}$, made from the acid by adding ammoniac hydrate, driving off the excess of ammonia on the water-bath, and precipitating with argentic nitrate, formed a

white mass made up of small needles. It was washed with water, dried *in vacuo*, and analyzed.

0.2686 gr. of the salt gave 0.1200 gr. AgCl.

	Calculated for $C_8H_6BrO_2Ag$.	Found.
Silver	33.54	33.62

It is slightly soluble in boiling water, freely in dilute nitric acid.

Calcic Orthobromalphatoluylate, $Ca(C_6H_4BrCH_2COO)_2$, made by boiling an aqueous solution of the acid with calcic carbonate, and evaporating the filtrate, gave, dried *in vacuo*, the following result:—

0.24969 gr. of the salt gave 0.0300 gr. CaO.

	Calculated for $(C_8H_6BrO_2)_2Ca$.	Found.
Calcium	8.54	8.58

It crystallizes from a very concentrated hot solution in circular groups of radiating needles, very soluble in water, somewhat less so in alcohol.

The *barium* salt formed an amorphous mass, like varnish.

A solution of the ammonium salt gave the following precipitates: with a salt of copper, *bluish green*; with ferric chloride, *orange brown*; with mercurous or plumbic salts, *white*; all of which resembled those obtained with the parabromalphatoluylic acid.

Orthobrombenzylsulphocyanate, $C_6H_4BrCH_2SCN$, is an oil which does not solidify in a freezing mixture of snow and salt. It was not analyzed.

Orthobrombenzylamines. The product of the action of alcoholic ammonia on orthobrombenzylbromide at 100° , for two hours, consisted of crystals of the tertiary amine, and a liquid containing the primary and secondary amines and ammonia, with their bromides. After filtering, the crystals were washed with cold alcohol, sodic hydrate, and finally water, and then recrystallized from warm ether till they gave a constant melting-point ($121\frac{1}{2}^\circ - 122^\circ$). The filtrate from the crystals was evaporated to dryness, and treated with carbonic dioxide to convert any free primary amine into carbonate. Upon washing with water, the salts of the primary amine and ammonia dissolved, leaving the secondary amine as an oil, which, after washing with sodic hydrate, was converted into the chlorplatinate by addition of chlorplatinic acid to its alcoholic solution. To the filtrate from the secondary amine, sodic hydrate was added, and the oily primary amine thus obtained washed with water until it was free from ammonia, care being taken not to expose it to the carbonic dioxide of the air.

Monorthobrombenzylamine, $C_6H_4BrCH_2NH_2$, is a colorless oil, insoluble in water, but soluble in ether, which absorbs carbonic dioxide from the air very readily, becoming converted into the carbonate.

The *carbonate*, made most easily by allowing an ethereal solution of the free base to evaporate in the air, forms small white crystals; melting-point, 95° ; and is soluble in water and alcohol.

The *chloride*, made by adding hydrochloric acid to the carbonate, crystallizes in white radiating needles, or from alcohol in small curled needles; melting-point, 208° ; and is soluble in water and alcohol.

The *chlorplatinate*, $(C_6H_4BrCH_2NH_3)_2PtCl_6$, is precipitated on adding chlorplatinic acid to the free base; an analysis gave

0.1990 gr. of substance gave 0.0505 gr. Pt.

	Calculated for $[C_7H_6BrNH_3]_2PtCl_6$.	Found.
Platinum	25.16	25.38

It forms indistinct orange-yellow needles, sparingly soluble in water, decidedly so in alcohol, and insoluble in ether.

The *Diorthobrombenzylamine* was made by treating the chlorplatinate with sulphuretted hydrogen, washing the chloride out of the platinic sulphide with hot alcohol, and precipitating the free base with sodic hydrate from the solid chloride. In this way an oil was obtained, which solidified after some time in well-marked rhombic crystals, with an agreeable smell, melting at 36° , and soluble in all the ordinary solvents, with the exception of water.

Diorthobrombenzylamine Chlorplatinate, $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$, prepared as already described, was purified by washing with alcohol and water, dried at 70° , and analyzed.

0.5840 gr. of the salt gave 0.1030 gr. Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Platinum	17.58	17.66

A yellow obscurely crystalline precipitate, slightly soluble in water and alcohol, insoluble in ether.

The *chloride* made by adding hydrochloric acid to an alcoholic solution of the free base separates out as the alcohol evaporates in groups made up of a few radiating white needles, which melt at 166° , are but slightly soluble in cold water, more soluble in hot and in alcohol, sparingly in ether.

Triorthobrombenzylamine, $(C_6H_4BrCH_2)_3N$, gave the following result on analysis:—

0.3245 gr. of substance gave 0.3488 gr. AgBr.

	Calculated for $(C_7H_6Br)_3N$.	Found.
Bromine	45.80	45.73

It forms small prisms with an adamantine lustre, melting at $121\frac{1}{2}^{\circ}$ – 122° and subliming in oily drops; almost insoluble in H_2O and alcohol; slightly soluble in cold, freely in hot ligroine, and in ether and benzol.

Triorthobrombenzylamine Chlorplatinate, $[(C_6H_4BrCH_2)_3NH]_2PtCl_6$, made by adding chlorplatonic acid to an ethereal solution of the amine, gave the following result on analysis:—

0.39708 gr. of the salt gave 0.0540 gr. Pt.

	Calculated for $[(C_6H_4Br)_3NH]_2PtCl_6$.	Found.
Platinum	13.51	13.60

A whitish yellow, barely crystalline precipitate, insoluble in water and ether, and very slightly, if at all, soluble in alcohol.

On boiling the tertiary amine with dilute alcohol and hydrochloric acid, it dissolved, and on cooling deposited white spheres made up of radiated needles; but an analysis of the substance gave an amount of chlorine too low for the pure chloride, and we did not think the compound of sufficient importance to study it further.